Glass and Ceramics, Vol. 71, Nos. 3 – 4, July, 2014 (Russian Original, Nos. 3 – 4, March – April, 2014)

UDC 666.76

ASSORTED CERAMIC ARTICLES FROM SILICON NITRIDE

E. B. Bendovskii[1]

Translated from *Steklo i Keramika*, No. 4, pp. 27 – 31, April, 2014.

A series of works on the development of technologies for manufacturing various articles from silicon nitride based materials is presented. These technologies make it possible to manufacture articles for a wide range of applications ranging from porous, permeable for the filtration of corrosive media, up to nearly the theoretical density for construction articles.

Key words: silicon nitride, manufacturing technology, articles.

More and more articles for the most diverse applications are now being manufactured from inorganic nonmetallic materials, commonly called ceramic. In the process there arise new problems whose solution requires materials either with new properties or new property indices. For this reason the range of compounds proposed for manufacturing articles is increasing. And, of course, oxygen-free compounds unavoidably fall into this range. Historically, compounds with high melting temperatures (carbides and nitrides of silicon, aluminum and transition metals) were at the top of this list.

Silicon nitride Si_3N_4, which is the only compound in the silicon—nitrogen system, exists in two polymorphic modifications. The silicon—nitrogen phase diagram is little studied, but it is customarily assumed that at 1900°C silicon nitride melts with decomposition. Since the self-diffusion coefficients of silicon and nitrogen in silicon nitride are of the order of 10^{-22} m^2/sec at 1400°C, the complexity of the manufacture of ceramic articles from silicon nitride becomes understandable. In addition, the combination of the indices of the chemical, mechanical and thermomechanical properties makes silicon nitride attractive for use as a refractory material with high specific performance properties [1].

The difficulties arising in the manufacturing of ceramics from silicon nitride make it necessary to resort to unconventional methods of sintering. Usually, sintering is done by the following methods:

1) reaction sintering — nitriding of silicon blanks under variable nitrogen pressure;

2) sintering using specially fabricated powders of silicon nitride with sintering additives under a wide range of sintering conditions: hot pressing, nitrogen gas pressure and charging.

[1] M. V. Lomonosov Moscow State University, Moscow, Russia (e-mail: bendovskyi.e.b@yandex.ru).

A series of works pertaining to all of the main stages of the manufacture of a ceramic body was set up and performed in order to develop technology for manufacturing ceramic parts for various applications:

1) preparation of powders;

2) synthesis; silicon nitride was fabricated, taking account of its particulars, in the form of power as well as a ceramic body (reaction-sintered silicon nitride RSSN);

3) fabrication of the molding body;

4) molding of the ceramic blank;

5) heat-treatment of the molded blanks.

PREPARATION OF POWDERS

Blocks of elemental silicon, which were comminuted to particle size about 1 mm and then milled under various conditions, were used in all work. In this connection there are two basic methods of manufacturing ceramic from silicon nitride: reaction sintering and sintering with special sintering additives; the silicon was milled in pure form and with sintering additives.

Since the aim of the entire complex of investigations was to develop technologies for manufacturing from silicon nitride ceramic articles for the most diverse applications, it was necessary to develop compositions of the molding bodies as well as methods of fabricating them for each particular type of article.

FABRICATION OF THE MOLDING BODY

Articles intended for furnace linings have a comparatively simple shape, and they can be mold by pressing special powders. In the case of bodies with a grainy composition with a binder comprised of reaction-sintered silicon nitride a

necessary condition for building strength during firing of silicon-containing bodies in a nitrogen atmosphere is the organization of a continuous matrix of compacted silicon powder into which separated grains of coarsely disperse filler are introduced in the course of the blank molding process. For this reason, in the case of monofractional filler the content (by weight) of the fine silicon was about 30%. Of course, the required amount of silicon depends on the filler density and can be reduced if the filler is polydisperse. In addition, for silicon nitriding temperatures 1200 – 1400°C the most commonly used fillers (silicon carbide, corundum, periclase and many grades of fireclay) remain inert to the initial silicon and to the silicon nitride formed. For this reason, the properties of the articles obtained are practically independent of the grain composition of the filler [2].

To obtain strong materials from grainy bodies with a binder consisting of reaction-sintered silicon nitride a continuous phase of the compacted silicon powder must be present in the compacted blank. The presence of such a phase makes it impossible to obtain grainy permeable structures.

To fabricate a permeable structure from reaction-sintered silicon nitride a matrix comprised of compacted silicon powder and a continuous channel-pore structure must be formed at the molding stage. This problem is solved by using a polyurethane foam (PUF) preform. This technology requires silicon-powder-based slip that is easily fabricated and safe to use. For this reason water was used as a dispersion medium.

In the course of the subsequent heat treatment the polyurethane foam present as a base burns up, forming hydrogen cyanide, among other substances. To exclude this extremely undesirable production waste based on granular powders a technology in which a matrix of compacted silicon powder and channel pores is formed simultaneously at the blank formation stage was proposed [3]. The technology includes as one alteration the fabrication of granules suitable for the formation of blanks.

Articles for use in construction are one of the proposed applications of densely sintered particles from silicon nitride. This makes it necessary to mold blanks of articles with a complex shape and precise dimensions. To solve this problem it is best to mold blanks by casting thixotropic suspensions (slips), specifically, hot casting of thermoplastic slips under pressure.

First and foremost, the slip must have a high concentration of a solid phase, which reduces the shrinkage occurring in the course of heat treatment and, in consequence, preserves the shape and dimensions and increases the yield of good parts. Another very important characteristic of slip is low viscosity for maintaining a high concentration of the solid phase. Low viscosity makes the molding process possible, i.e., it imparts to the molding body the required shape by having it fill the mold.

The problems formulated above were solved for silicon and silicon nitride powders. Compositions of temporary binders and techniques for preparing slips, making it possible, for example, to obtain apparent density of the silicon powder up to 0.712%, which corresponds to porosity of the blank 28.8%, were developed. The casting properties of slip are acceptable. In addition, the techniques proposed for making slip make it possible to increase by 25 – 40% the properties of ceramic articles, for example, the mechanical and electric strength. No less important is a reduction of the confidence interval for the properties by a factor of 2 – 3 [4].

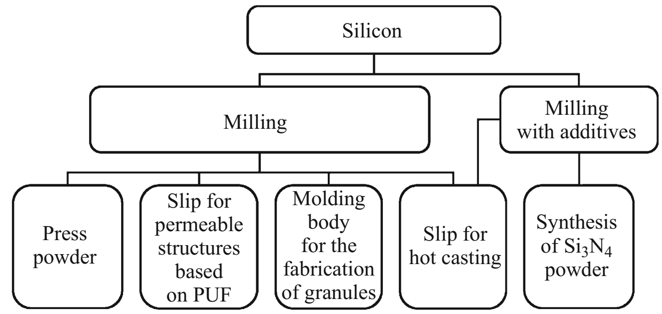

Fig. 1. Diagram showing the preparation of the molding bodies for fabricating articles from silicon nitride.

A diagram of the fabrication of molding bodies for obtaining articles from silicon nitride is presented in Fig. 1.

FORMATION OF A CERAMIC BLANK

Blanks are formed from bodies with a grainy composition by means of the standard semi-dry pressing techniques. This process is in no way different from the formation of blanks from conventional materials.

As far as the formation of articles with a permeable structure from granular powders is concerned, for granules smaller than 0.5 mm a permeable structure is formed in the course of heat treatment without taking any special measures. For granules larger than 0.5 mm a reliable contact is already required between neighboring granules at the formation stage.

This problem was solved by varying the composition of the temporary binder and the processes conducted during formation.

Success in forming blanks from thermoplastic slips is attained mainly by the presence of slip with reliable properties. At the same time no less important are the conditions under which the slip fills the mold. For this reason the formation problems were solved as a single package: slip – mold-filling process and parameters – mold construction.

HEAT TREATMENT OF MOLDED BLANKS

Sometimes, excepting hot pressing, it is convenient of divide the heat treatment processes leading to the fabrication of a ceramic body based on silicon nitride into three groups.

1. *Reaction sintering* — the elemental silicon present in the initial batch transforms when heated in a nitrogen atmosphere into silicon nitride, strengthening the blank.

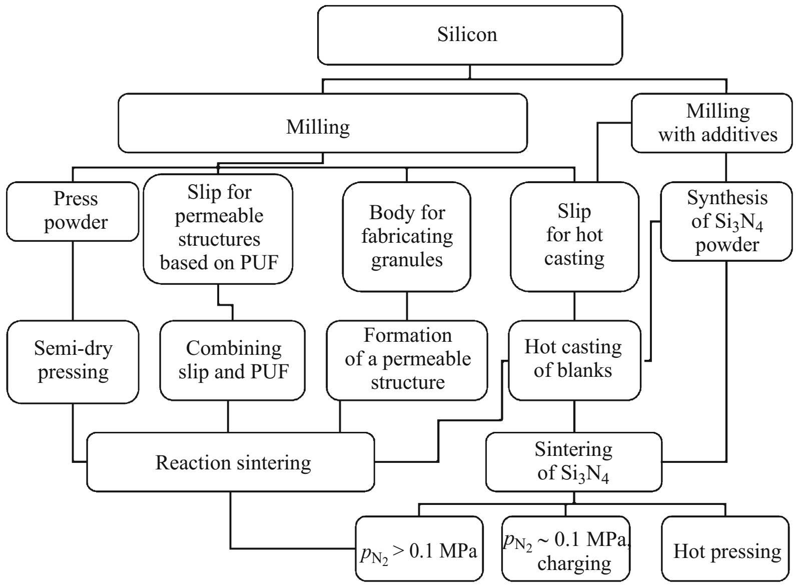

Fig. 2. The scheme used for molding and heat-treating ceramic blanks.

2. *Sintering of blanks made from silicon nitride with specially introduced sintering additives.* The additives can be introduced at different stages of the ceramic fabrication process.

3. *Combining the first two techniques*, where at the first stage of heat treatment the molded silicon article is nitrided and the nitride part is fired under variable nitrogen pressure. This combination is very attractive, since there is no shrinkage on nitriding, and the porosity decreases appreciably and therefore the shrinkage decreases at the final stage. Thus, the total shrinkage of the article is appreciably less than during firing of parts molded from silicon nitride powder.

The scheme for molding and heat-treating ceramic blanks is presented in Fig. 2.

Parts with a permeable semidry-pressed structure, molded by casting from silicon powder, were fabricated by means of reaction sintering.

A ceramic was fabricated by hot pressing, sintering under nitrogen pressure $p_{N_2} > 0.1$ MPa and sintering with charging under nitrogen pressure $p_{N_2} = 0.1$ MPa, from synthesized silicon nitride powders containing additives.

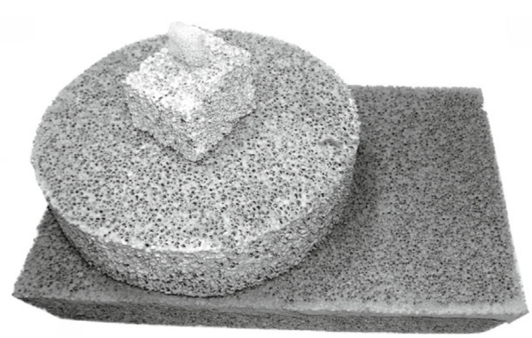

Fig. 3. Ceramic articles with permeable structure based on polyurethane foam with different composition (silicon nitride – second from the top).

The different methods of sintering are determined by the mold, the article's dimensions and the possibilities of the method. For example, hot pressing greatly limits the possibilities of fabricating articles with a complex shape. Sintering at elevated nitrogen pressures requires very specific and complex equipment. In the search for less complicated variants of firing work including firing of blanks in a charge at nitrogen pressure 0.1 MPa was performed.

Articles fabricated by semi-dry pressing from bodies with grainy composition operate successfully as lining in diverse heated units, including under very corrosive conditions, for example, lining of electrolyzers for obtaining aluminum and liners for melting furnaces. As a rule, the lining no longer causes malfunctioning of a plant.

Articles obtained from silicon nitride on the basis of polyurethane foam (Fig. 3) possess very high permeability to liquids and gases (hundreds of microns in a square). They were initially developed and successfully used as filters or metal melts. It should be noted that it is extremely important that if the filters based on oxide materials are one-time-use only, the filters based on silicon nitride can be used multiple times. The use of PUF as a mold makes it possible to fabricate permeable ceramic structures from practically any materials. This opens up the possibility of using articles for the most diverse applications, for example as carriers of catalysts for diverse processes, foundations for biomaterials, articles for medical applications and much else.

The use of granulated powders for molding permeable ceramic structures (Fig. 4) also makes it possible to fabricate articles with very high permeability from practically any materials with the possibility of the most diverse applications.

Articles based on reaction-sintered silicon nitride which are molded by hot casting (Fig. 5) operate successfully in

Fig. 4. Ceramic articles with permeable structure based on granulated powders with different composition.

Fig. 5. Hot-cast ceramic articles from reaction-sintered silicon nitride.

very corrosive media, such as metal melts, in the most diverse application — crucibles, jackets for thermocouples, funnels, pipes for transporting melts and many other uses. In addition, there were no cases of articles malfunctioning because of wear, except in situations with random mechanical action, for example, impacts.

By varying the conditions for the synthesis of silicon nitride powder it is possible to change over very wide limits the properties of the product obtained. For example, it is possible to prepare powder with α silicon nitride to 98%. At the same time under certain conditions crystals of â silicon nitride up to 10 μm in size grow at temperatures 1200 – 1400°C in the course of an α–β polymorphic transformation, even for very small self-diffusion coefficients of silicon and nitrogen, though ordinarily β silicon nitride formed in the course of a polymorphic transformation during a reaction of silicon with nitrogen is obtained in the form of accumulations of very small (< 1 μm) crystals [5].

Hot pressing was used to fabricate from silicon nitride powder the working bodies of cam followers in internal combustion engines (ICE) (Figs. 6 and 7). Testing of the fabricated followers showed that they attach successfully with the

Fig. 6. Hot-pressed blanks from silicon nitride.

Fig. 7. Ready cam follower with working body made from hot-pressed silicon nitride.

cam of the distributing drive shaft and are serviceable under the actual operating conditions of an engine. In addition, the wear of a ceramic working body is an order of magnitude less than for a conventional body, and the coefficient of friction is several-fold less than for a conventional pair.

Articles made from silicon nitride by sintering under nitrogen pressure > 0.1 MPa and in a charge under nitrogen pressure 0.1 MPa have porosity 90 – 98%. The ultimate strength in bending of such articles is consistently 550 MPa. Samples with ultimate strength in bending to 800 MPa were fabricated in a number of experiments. Such results make it possible to hope for strengthening of equipment for heat-treating parts. A working wheel of a turbo compressor in ICE successfully tested for its serviceability in the exhaust line of a real engine is displayed in Fig. 8 [6].

In summary, a series of technologies making it possible to manufacture from materials based on silicon nitride articles with different structure and applications ranging from highly permeable to high density and from refractory to structural was developed and implemented.

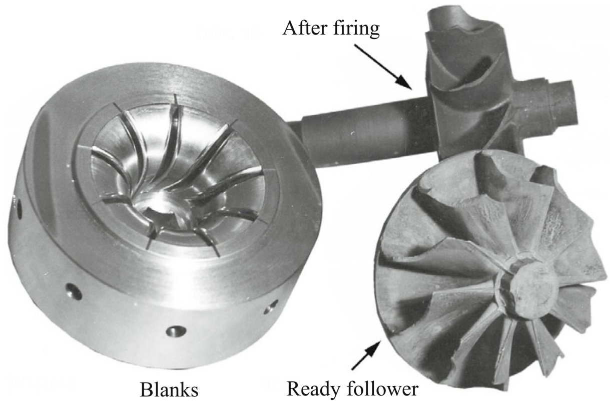

Fig. 8. Working wheel of a turbo compressor made from heavy-sintered silicon nitride.

REFERENCES

1. R. A. Andrievskii, "Silicon nitride, synthesis and properties," *Usp. Khim.*, **64**(4), 311 – 329 (1995).
2. E. B. Bendovskii, I. Ya. Guzman, and Z. F. Safiullina, "Properties of composite materials in binder from reaction sintered silicon nitride," *Ogneupory*, No. 4, 13 – 16 (1984).
3. E. B. Bendovskii and I. Ya. Guzman, "Formation of permeable ceramics with a granular structure," *Steklo Keram.*, No. 11, 13 – 14 (2004); E. B. Bendovskii and I. Ya. Guzman, "Formation of permeable ceramics with a granular structure," *Glass Ceram.*, **61**(11 – 12), 367 – 370 (2004).
4. E. S. Bendovskii and Yu. M. Mosin, "Influence of shaping method on the strength of ceramics," *Steklo Keram.*, No. 11 – 12, 27 – 29 (1992); E. S. Bendovskii and Yu. M. Mosin, "Influence of shaping method on the strength of ceramics," *Glass Ceram.*, **49**(11 – 12), 523 – 526 (1992).
5. E. B. Bendovskii and I. Yu. Guzman, "Particulars of nitriding of silicon," *Steklo Keram.*, No. 11, 22 – 26 (2003); E. B. Bendovskii and I. Yu. Guzman, "Specifics of Silicon Nitration," *Glass Ceram.*, **60**(11 – 12), 374 – 378 (2003).
6. E. B. Bendovskii, "Silicon nitriding at different nitrogen pressures," *Steklo Keram.*, No. 10, 6 – 11 (2012); E. B. Bendovskii, "Silicon nitridation at different nitrogen pressures," *Glass Ceram.*, **69**(9 – 10), 324 – 329 (2012).